Dissociative Ionization and Heat of Formation of OBrO	U11

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With the exception of bromine monoxide, knowledge of the thermochemical properties of the higher bromine oxides is scarce. Specifically, for bromine dioxide, OBrO, there have been only inaccurate estimates for heat of Formation, Δ_fH(OBrO) = 122 kJ mol^{-1}; a bona fide experimental value does not exist. Yet, an accurate, experimentally determined value is urgently needed so that an evaluation of the role of OBrO reactions in stratospheric nightime chemistry can be made.

By using the discharge flow-photoionization mass spectromer apparatus at U11, a large number of experiments were performed to obtain an appearance energy (AE) for the dissociative ionization of OBrO. All of these experiments yield a threshold at about 101 $\pm$1 nm which gives an AE of 12.2 $\pm$0.1 eV. This AE, in turn, yields a Δ_fH(OBrO) of 220 $\pm$10 kJ mol^{-1} or 52.6 kcal mol^{-1}. With such a wide range of values for the heat of formation of OBrO, it will be important to pursue the PIMS experimental work to obtain a definitive result.